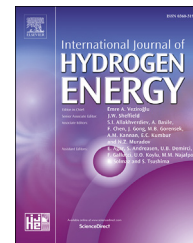




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# Enhanced activity of CO<sub>2</sub> methanation over mesoporous nanocrystalline Ni–Al<sub>2</sub>O<sub>3</sub> catalysts prepared by ultrasound-assisted co-precipitation method

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## ABSTRACT

The ultrasound-assisted co-precipitation method was employed for the synthesis of the Ni–Al<sub>2</sub>O<sub>3</sub> catalysts with different metal loadings for the CO<sub>2</sub> methanation reaction. This study indicated that increasing the Ni loading up to 25 wt.% enhanced the surface area, decreased the crystallinity and improved the reducibility of the catalysts, while further raise in Ni loading adversely influenced the surface area. Improvements in catalytic performance were obtained with the raise in Ni content because of enhancing the BET area. The results confirmed that the 25Ni–Al<sub>2</sub>O<sub>3</sub> catalyst with the highest BET area (188 m<sup>2</sup> g<sup>−1</sup>) and dispersion of Ni has the highest catalytic activity in CO<sub>2</sub> methanation and reached to 74% CO<sub>2</sub> conversion and 99% CH<sub>4</sub> selectivity at 350 °C. In addition, this catalyst exhibited a great stability after 10 h time-on-stream.

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## Introduction

In recent years, various methods for reducing the amount of carbon dioxide in the atmosphere are being considered because of increasing CO<sub>2</sub> emissions through the combustion of fossil fuels for energy supply, which affects the global warming, precipitation patterns, ocean acidification, and weather patterns [1–3]. Hydrogen has been distinguished as an energy carrier which can be generated by the water electrolysis using power generated from renewable energy systems. However, there are still difficulties in the utilization of

H<sub>2</sub>. The use of hydrogen has been limited due to the requirements of infrastructures for its distribution, storage, and transportation. The potential alternative is CH<sub>4</sub>, which is a main component of the natural gas and is of significant importance to the industry, energy, and transportation sectors worldwide [4–7].

The methanation of carbon dioxide (CO<sub>2</sub> + 4H<sub>2</sub> → CH<sub>4</sub> + 2H<sub>2</sub>O, ΔH = −165 kJ/mol), is a reaction of great potential technological and environmental importance because its usage as chemical storage of the excess H<sub>2</sub> generated from renewable energy sources such as solar energy, hydropower,

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and biomass. This reaction can also reduce the CO<sub>2</sub> emissions (greenhouse gas) from the atmosphere [8–10].

A thermodynamic analysis shows that CO<sub>2</sub> methanation reaction is a highly exothermic reaction and favors formation of methane at high pressure and low temperature. However, due to kinetic limitations is difficult to achieve the high reaction rate for this reaction with high selectivity [11]. Therefore, the catalytic CO<sub>2</sub> methanation has been investigated over the VIII B based metals (Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt) catalysts on various carriers (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, TiO<sub>2</sub>) [12–19]. Among a large number of catalysts investigated for the reaction, the Ni-based catalysts are widely used for methanation reaction due to acceptable activity and competitive price. However, these catalysts suffer from sintering and serious carbon accumulation at high temperatures [20–23]. The catalytic performance strongly depends on the type of the catalyst carrier due to the influence of the carrier on the active phase dispersion, formation of inactive spinel phases, etc. Al<sub>2</sub>O<sub>3</sub> is the most common catalyst carrier due to its low cost, high specific surface area, porous structure, and good thermal stability leading to high catalytic activity [24]. The catalytic performance of the nickel based catalysts is influenced by several factors such as Ni content, type of promoters and carriers, catalyst synthesis method, etc [25,26]. The interaction of the metal with catalyst carrier can influence the dispersion of metal, crystal structure, and allowable metal loading. The catalyst preparation procedure is one of the main factors that affect the physicochemical characteristics of the Ni-based catalysts. There are several methods for the preparation of Ni-based catalysts such as impregnation, co-precipitation, the fusion method, the solution-spray plasma technique, sol-gel, etc [10,27,28]. For example, He et al. [29] prepared the Ni–Al hydrotalcite derived catalyst (Ni–Al<sub>2</sub>O<sub>3</sub>-HT) by co-precipitation method and the catalyst exhibited a high CO<sub>2</sub> conversion of 82.5% and CH<sub>4</sub> selectivity of 99.5% at 350 °C, which was higher than the sample prepared by impregnation method. Recently, the studies have been concentrated on the preparation of the nanomaterials and nanostructured supported metal catalysts. The homogenous dispersion of nanoparticles enhances the activity of catalyst by imparting a large number of active centers and enhances the stability by prevention of coke deposition [30,31]. Song et al. [32] prepared the well-dispersed Ni/Al<sub>2</sub>O<sub>3</sub> catalyst with a microwave-assisted method, which showed high catalytic activity and stability for the CO<sub>2</sub> methanation. Ultrasonic techniques have been extensively used as an efficient method for preparation of homogenous and dispersed nanoparticles [33–35]. The sonochemical effects stemmed from acoustic cavitation phenomenon. Ultrasound irradiations included compression and rarefaction cycles and generate cavitation bubbles in liquids or solutions. When liquids are irradiated with ultrasound in the process of cavitation, the cavitation bubbles produced during rarefaction cycles and after several compression cycles, the implosive collapse of cavitation bubbles occurred which lead to an intense increase in local temperature (up to 5000 °C) and pressure (2000 atm). In addition, ultrasound irradiations produce free radicals which increase reaction rates at ambient temperatures. As a consequence, these unique conditions lead to the formation of homogenous nanoscale particles with high surface area [33,36]. Compared with conventional methods,

sonochemical synthesis has advantages such as the production of nanocrystals with narrow size distribution and high purity, reduction of particles growth and their agglomeration, decreasing of phase transformation temperature, and control in size and morphology [37]. In our previous work, we reported that the nickel aluminate catalyst prepared by the ultrasound assisted co-precipitated method had higher BET area and smaller crystallite size compared to the catalysts synthesized by the impregnation and non-ultrasound assisted co-precipitated methods [38].

In this research work, the influences of Ni content on the catalytic behavior of Ni-based catalysts in CO<sub>2</sub> methanation reaction are reported. The content of nickel can affect the dispersion and the interaction of nickel with the catalyst carrier [39,40].

In this article, Ni–Al<sub>2</sub>O<sub>3</sub> catalysts with various Ni loadings were synthesized by ultrasound assisted co-precipitated method and the catalytic characteristics of the prepared samples were studied in CO<sub>2</sub> methanation.

## Experimental

### Catalyst preparation

The preparation method of the catalysts was reported in our previous work. Ni–Al<sub>2</sub>O<sub>3</sub> catalysts with various Ni contents (15 wt.%, 20 wt.%, 25 wt.% and 33 wt.%) were synthesized by the ultrasound assisted co-precipitated method. Briefly, a solution of NaOH (1 M) was added dropwise into a mixed solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98% purity, Merck) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98% purity, Merck) with calculated ratios at room temperature under 70 W ultrasonic (QSONICA-Q700 Sonicator) output powers to set the pH to 10. After this step, the slurry was filtered and washed with hot distilled water to eliminate the Na<sup>+</sup> cation. The resulted filter cake was dried and subsequently calcined at various temperatures for 4 h.

### Catalytic reaction

The CO<sub>2</sub> methanation reaction was evaluated in a tubular fixed-bed flow reactor (i.d. 10 mm) made of quartz. 200 mg of the sieved (35–60 mesh) catalyst was loaded into the reactor. The temperature was controlled by a thermocouple installed in the bottom of the catalyst bed. Before the reaction, the catalyst was reduced in pure H<sub>2</sub> flow with a flow rate of 25 ml/min at 600 °C for 2 h. After cooling to the reaction temperature (200 °C), the feed gas mixture containing CO<sub>2</sub> and H<sub>2</sub> at the desired ratio was passed continuously through the catalyst. The gas products were monitored by a gas chromatograph (Varian, model 3400) equipped with a TCD and a Carboxen 1000 column. The CO<sub>2</sub> conversion ( $X_{CO_2}$ ) and the selectivity of CH<sub>4</sub> ( $S_{CH_4}$ ) were determined by the following equation:

$$X_{CO_2}(\%) = \left(1 - \frac{CO_2}{CH_4 + CO + CO_2}\right) \times 100 \quad (1)$$

$$S_{CH_4}(\%) = \left(\frac{CH_4}{CH_4 + CO}\right) \times 100 \quad (2)$$

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